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Mechanical, Thermal and Biodegradable Properties of Bioplast-Spruce Green Wood Polymer Composites

A. Atli, K. Candelier, J. Alteyrac

***Abstract*—**Environmental and sustainability concerns push the industries to manufacture alternative materials having less environmental impact. The Wood Plastic Composites (WPCs) produced by blending the biopolymers and natural fillers permit not only to tailor the desired properties of materials but also are the solution to meet the environmental and sustainability requirements. This work presents the elaboration and characterization of the fully green WPCs prepared by blending a biopolymer, BIOPLAST® GS 2189 and spruce sawdust used as filler with different amounts. Since both components are bio-based, the resulting material is entirely environmentally friendly. The mechanical, thermal, structural properties of these WPCs were characterized by different analytical methods like tensile, flexural and impact tests, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD). Their water absorption properties and resistance to the termite and fungal attacks were determined in relation with different wood filler content. The tensile and flexural moduli of WPCs increased with increasing amount of wood fillers into the biopolymer, but WPCs became more brittle compared to the neat polymer. Incorporation of spruce sawdust modified the thermal properties of polymer: The degradation, cold crystallization, and melting temperatures shifted to higher temperatures when spruce sawdust was added into polymer. The termite, fungal and water absorption resistance of WPCs decreased with increasing wood amount in WPCs, but remained in durability class 1 (durable) concerning fungal resistance and quoted 1 (attempted attack) in visual rating regarding to the termites resistance except that the WPC with the highest wood content (30 wt%) rated 2 (slight attack) indicating a long term durability. All the results showed the possibility to elaborate the easy injectable composite materials with adjustable properties by incorporation of BIOPLAST® GS 2189 and spruce sawdust. Therefore, lightweight WPCs allow both to recycle wood industry byproducts and to produce a full ecologic material.

***Keywords*—**Biodegradability, durability, mechanical properties, melt flow index, spectrophotometry, structural properties, thermal properties, wood-plastic composites.

I. Introduction

THE possibility to modify polymer properties by incorporation of fillers has been known for a while [1]. The fillers with different sizes, shapes and chemical natures have been inserted into different polymer matrix for different purposes [2]. The polymers used are mainly thermoplastics and the fillers are mainly inorganic materials like oxides (MgO, Al_2O_3, ZnO,…) [3]-[7], silicates (talc, mica, kaolin, montmorillonite….) [8]-[10] or metals (boron, steel,…) [11]. The petroleum based nature of the commonly used thermoplastic polymers, the heavier character of the inorganic filler compared to the polymer matrix as well as their non-sustainable nature are the disadvantages of the composites made by synthetic petroleum based thermoplastic polymer and inorganic fillers.

Environmental awareness and reduction of the resources issued from petroleum have triggered an enormous interest to manufacture ecofriendly parts. Wood satisfies the sustainability requirements and is able to substitute some existing materials when used as filler [12].

Wood contains biopolymers such as lignin, cellulose and hemicellulose [13]. Its stiffness, toughness and robustness due to its chemical structure and anatomy make it a performant material. From a polymer composite standpoint, wood is less expensive, abundant in nature, lightweight, environmentally friendly, stiffer and stronger than many commodity synthetic polymers, turning it into a suitable material to fill and reinforce them.

The polymer matrix used for WPCs has to be processed below 200 °C to prevent any major modification into the wood structure and composition [14]. This thermal limitation was one of the reasons why the polymers commonly used in WPCs were polyolefin like poly(ethylene) (PE) [15], poly(propylene) (PP) [16] or poly(vinyl chloride) (PVC) [13] [17] having a melting temperature below 200 °C. Nevertheless, the petroleum based and the unsustainability nature is the main inconvenience of these polymers. As an alternative, biopolymers can be processed as matrix in WPCs. Wood filler reinforced biopolymer composites have many advantages not only on the economical point of view since wood byproducts are inexpensive, available, and lightweight but also for its low environmental impact due to their minimal health hazards, renewability and biodegradability. Composites made in such a way can profit the classical shaping process of polymers like injection molding for the production of fully ecofriendly composite materials.

BIOPLAST® GS 2189 is a plasticizer-free thermoplastic material that contains polyester and starch which is biological sourced material. The bio based carbon share of the entire formulation reaches 69% and it is completely biodegradable in an industrial composting environment. Its melting temperature below 200 °C and easy flowing are therefore particularly suitable for processing by injection molding to produce items that are environmentally compatible.

This work shows the possibility to make the fully eco-friendly wood-biopolymer composites by blending a

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commercial biopolymer, BIOPLAST® GS 2189 and spruce sawdust. The mechanical, structural, thermal, rheological, decay and termite resistance properties of WPCs were studied by several analytical methods for different amount of incorporated wood filler into the biopolymer.

II. Experimental

A. Raw Materials for Sample Preparation

The polymer, BIOPLAST® GS 2189, was supplied by the BIOTEC GmbH & Co. KG Company (Germany). The manufacturer mentions that it is a bio sourced material with a Melt Flow Index (MFI) of 35 g/10 min (190°C, 2.16 kg) and a density of 1.35 g/cm^3 [18]. BIOPLAST® GS 2189 is particularly suitable for processing by injection molding and completely biodegradable in an industrial composting environment.

The raw spruce byproduct was provided by a local sawmill. The sawdust was screened with a sieve having nominal squared opening cells of 400 µm.

B. Sample Preparation

The BIOPLAST® GS 2189 polymer pellets and raw spruce sawdust were dried at 103 °C during 24 hours prior to blending. They were then mixed in a Brabender blender at 180 °C. The sawdust was added into the molten polymer in the mixer bowl of 35 cm^3. The torque generated by two rotating blades with adjustable speed was recorded as a function of time during blending and the blades were kept at constant torque for approximately 10 min after the torque was stabilized. Six batches were prepared in order to have enough volume to produce approximately 15 samples for each composition. After blending, the obtained pads were grinded and injected by using an ARBOURG AllRounder 270S injection mold with an 18 mm diameter screw. The typical temperatures during injection molding set to 155-180 °C, with a cooling time of 15 seconds. Injection flow rate was fixed to 30 cm^3/sec with a pressure of 1200 bars. The mold was kept at room temperature. The tensile test samples and small rods of 4 mm x 10 mm x 100 mm have been obtained for different analysis as shown in Fig. 1.

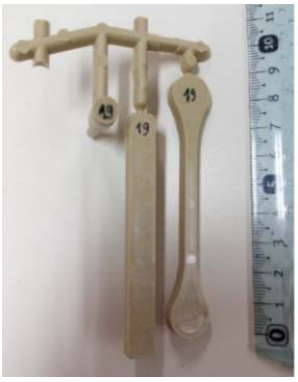

Fig. 1 Injected rod shaped and tensile test WPC samples

C. Methods

The tensile tests were performed on the samples (specially shaped for this purpose) with a Shimadzu AGS-X apparatus equipped with a camera extensometer for displacement measurements at room temperature. The pulling speed was 5 mm/min.

The three point bending tests were carried out on the samples having a rod shape by using the same apparatus for the tensile tests. Nevertheless the usual grips were replaced by the special design for flexural test. The moving head speed for loading was 1 mm/min.

The IZOD impact tests were conducted by a CEAST apparatus at room temperature on the rod shaped unnotched samples (Fig. 1). The mechanical properties of WPC samples were compared to those of neat BIOPLAST® GS 2189.

Wide Angle XRD experiments were carried out in an INEL Diffractometer by using a Cobalt source (1.789 Å, 25 KV, 25 mA). X-Rays were detected by a 120° hemispherical multichannel detector.

OLYMPUS BX51 and OLYMPUS DSX500 optical microscopes were used to realize the images on sample surfaces. The second microscope equipped with an upright motorized system allowed to obtain 3D images.

A Philips XL30i Scanning Electron Microscope (SEM) was also used for the observation of the sample. Elemental characterization within the SEM was assessed by Energy Dispersive X-ray spectroscopy (EDX).

TA instruments Q50 apparatus was employed for TGA under nitrogen flow of 90 mL/min with a heating rate of 10 °C/min. For DSC analysis, a TA Instruments Q20 was used under nitrogen ambient (50 mL/min) with 10 °C/min.

Melt Flow Index (MFI) of pure polymer and wood composites was realized at 180 °C with a mass of 2.16 kg during 30 seconds and the results were extrapolated to the common MFI unit g/10 min. An average value was calculated over three experiments of 30 seconds.

The color analysis was performed by a Minolta cr200 color analyzer by measuring the reflected light from the WPCs. A white polystyrene pad was used to calibrate the system and employed as a background on which the specimens were placed during the color measurements. The L*, a* and b* coordinates measured on the polystyrene pad background were 97.28, -0.3 and -0.12 respectively. As a reminder, L* indicates lightness (0: black; 100 white), a* shows red-green contribution (positive values: red; negative values: green; neutral: 0) and b* designates blue-yellow contribution (positive values: yellow; negative values: blue; neutral: 0).

The water absorption tests were carried out on the rod shaped samples by using the distilled water at room temperature. Prior to the experiments, the samples were dried at 103 °C during 24 hours and cooled down to room temperature. All the samples were soaked at the same time into the distilled water provided by Laboratoire Aguettant (France) and removed from the water at the same time with specific intervals. They were blotted with a tissue paper to remove the excess surface water and weighed by a Mettler AE166 Delta range microbalance. They were then immersed again in the same distilled water for further measurements. Three samples were tested for each composition of WPCs. As

all the samples were obtained by injection in same mold, their dimensions were assumed to be very similar, then the water absorption results were able to be compared between them. Neat BIOPLAST® GS 2189 specimens injected were used as the reference. Three other spruce samples cut from a bulk spruce piece with a similar thickness as WPCs were also studied for comparison. The mass change (MC in %) due to the water absorption (WA) was estimated on a dry mass basis from:

$$MC\ (\%) = \left|\frac{m-m_0}{m_0}\right| x100 \quad (1)$$

where m is the mass at a given time, m_0 is the initial dried mass of the samples. The mass change calculated by using (1) was written in absolute value since it was used either for mass gain (the case of WA) or mass loss (the case of termites and fungal resistance).

WPCs with surrounding dimensions of 25 x 5 x 5 mm^3 (Length x Width x Thickness) were exposed to termites (*Reticulitermes flavipes*, ex. *santonensis*) and rot fungus in non-choice screening tests to examine the termite and fungal resistances. Beech (*Fagus sylvatica*) and pine sapwood (*Pinus sylvestris*) samples of dimensions 30 x 10 x 5 mm^3 were also tested against termite as controls. Prior to the test, each WPC sample and control samples were dried at 103 °C in order to obtain their anhydrous mass (m_0). For each set of composites and controls, three replicates were tested for their resistance against termites. Each specimen was placed in the middle of a 9 cm diameter Petri dish containing 40 g of Fontainebleau wet sand (4 vol. of sand/1 vol. of deionized water). A total of 50 termite workers, one nymph and one soldier were then introduced into each test device. These test devices were placed in a dark climatic chamber kept at 27 °C and >75% RH for 4 weeks. Observations were carried out on a weekly basis in order to add water and check termite behavior. At the end of the exposure, the samples were removed, cleaned of sand and termite survivors were counted. Sample degradations were given a visual rating according to the criteria of EN117 (2013) (the criteria being adjusted to the sample size). Then, the samples were dried at 103 °C to obtain their anhydrous mass and their mass change as Mass Loss (ML) was calculated according to (1) where m represents the anhydrous mass after termite exposure and cleaning of sand and termites survivors.

Sterile culture medium (65 ml), prepared from malt extract (40 g) and agar (20 g) in distilled water (1 L), was placed in a 72 cl volume glass bottle, closed with carded cotton inoculated with two small piece of mycelium of a freshly grown culture of two brown-rots [*Coniophora puteana* (CP) (BAM ebw. 15); *Poria placenta* (PP) (FPRL 280); and one white-rot [*Coriolus versicolor* (CV) (CTB 863 A)]. The inoculated Petri dishes were incubated for 2 weeks at 27 °C and 70% RH until malt extract agar was covered by mycelium. WPCs and control specimens were supported on sterile inert mesh to prevent contact with culture medium. All test samples previously oven dried at 103 °C to constant mass (m_0 in (1)) were γ-ray-sterilized and three specimens and one control sample were placed in each test device under sterile conditions. All wood polymer composite modalities were triplicated and the incubation was carried out for 8 weeks at 22 °C under controlled humidity conditions of 70% RH in a climatic chamber. At the end of the test exposure, mycelia were removed and all samples were oven-dried to constant mass at 103 °C. The extent of the fungal attack was determined based on the percentage of ML which was expressed as a percentage of the initial oven-dried mass of composite samples according to (1), m_0 is the oven dried mass before fungal test and m is dried mass after fungal test and cleaning.

The classification of WPCs decay resistances was determined according to the median values of ML (X), as specified in the XP Cen/TS 15083-1 (2006) standard (Table I). However, the analysis of all ML results obtained has been conducted on their minimum, maximum, average and mean values.

TABLE I
DURABILITY RATING SCALE ACCORDING TO XP CEN/TS 15083-1 (2006)

Durability class	Description	X (median values ML in %)
1	Very durable	X<5
2	Durable	5<X<10
3	Moderately durable	10<X<15
4	Slightly durable	15<X<30
5	Not durable	X>30

III. RESULTS AND DISCUSSION

A. Characterization of Raw Materials: BIOPLAST® GS 2189 and Spruce Sawdust

The WPC samples were prepared by incorporation of spruce sawdust into the BIOPLAST® GS 2189 used as polymer matrix. The real chemical composition of BIOPLAST® GS 2189 is unknown since it is not given by the industrial polymer supplier. The datasheet only indicates that the BIOPLAST® GS 2189 contains 75% of renewable raw material and has a biobased carbon share of 69% [18]. A more accurate characterization was then necessary prior to this study.

A few work found in the literature pointed out that the BIOPLAST® GS 2189 contains poly(lactic acid) (PLA) and potato starch [19]-[24].

A TGA thermogram obtained on neat BIOPLAST® GS 2189 showed typical slope changes highlighting the presence of several zones: a first weight loss zone between around 200 and 330 °C, a second weight loss zone between 330 and 410 °C and a third weight loss zone from 410 to 710 °C (Fig. 2). This is consistent with the results of Santos et al. [22] who have found, in their TGA thermogram, a first zone between 280 and 330 °C which was attributed to the degradation of PLA followed by a second zone above 330 °C attributed to the beginning of starch decomposition. The degradation at higher temperatures would come from possible mineral waste present in the starch [22] or additives or plasticizers [24]. The present TGA thermogram on neat BIOPLAST® GS 2189

was similar to the results found in the literature [22]-[25].

The TGA scan of neat BIOPLAST® GS 2189 allowed to detect a thermal residue of around 19% at 560 °C and around 10% at 800 °C.

The EDX analysis performed on the residue collected after TGA experiments of neat BIOPLAST® GS 2189 obtained after curing to 560 and 800 °C revealed the presence of calcium, oxygen and carbon peaks (Fig. 3). This figure displays also a picture taken on the residue obtained after heating up the neat polymer to 560 °C and also the atomic percentage of O and Ca (inset).

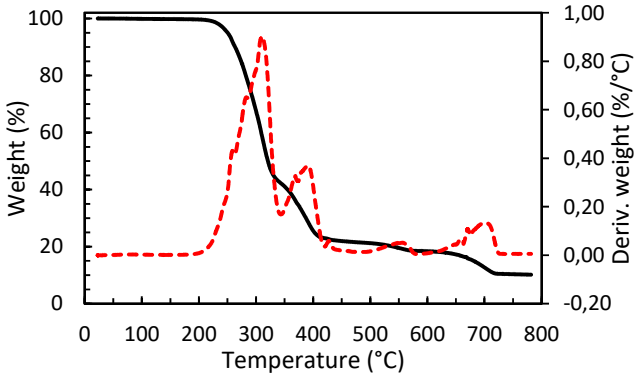

Fig. 2 TGA of neat BIOPLAST® GS 2189 and derivative of the TGA signal (dotted line)

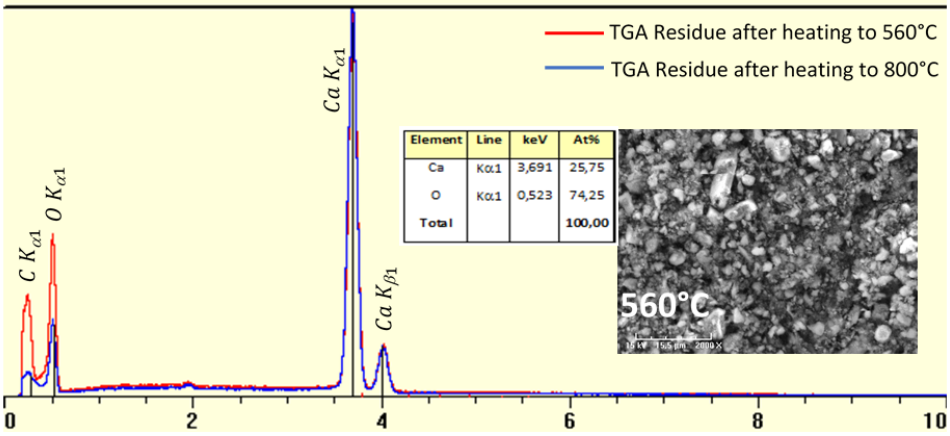

Fig. 3 EDX analysis of the TGA residue of neat BIOPLAST® GS 2189 obtained after heating to 560°C and 800°C. The atomic % of Ca and O was done on the table and a SEM picture of the TGA residue obtained after heating to 560°C (inset)

The XRD diffractogram realized on the residue obtained after curing the neat polymer to 560°C exhibited the sharp diffraction patterns (Fig. 4) corresponding to $CaCO_3$ (ICCD card number 47-1743). An atomic Ca/O ratio of 1/3 in EDX analysis (Fig. 3) and sharp XRD patterns corresponding to $CaCO_3$ as well as the particle nature of the residue would indicate that the BIOPLAST® GS 2189 was filled with $CaCO_3$ particles. It is well known that the $CaCO_3$ particles are extensively used as filler in polymers [26], [27]. But $CaCO_3$ thermally decomposes and the decomposition takes place between 635 and 835 °C according to the reaction $CaCO_3 \rightarrow CaO+CO_2$ [28]. This would be the reason why the oxygen and carbon peaks in EDX are relatively more intense (with respect to Ca $K_{\alpha 1}$ peak) for the residue heated up to 560 °C compared to that heated up to 800 °C. In TGA, the weight of the residue is around 19% at 560 °C and 10% at 800 °C. If the residue at 560 °C was totally originated from $CaCO_3$ (molecular weight is 100.07 g/mol), and the residue at 800 °C was totally originated from CaO (molecular weight is 56 g/mol), then the relative weight of the residue at 800 °C would be 19%(56/100.07)=10.6% which is consistent with the measured weight residue of 10% at 800 °C in our TGA experiment. This observation indicates that the Bioplast is filled by $CaCO_3$ with an amount of 19wt%.

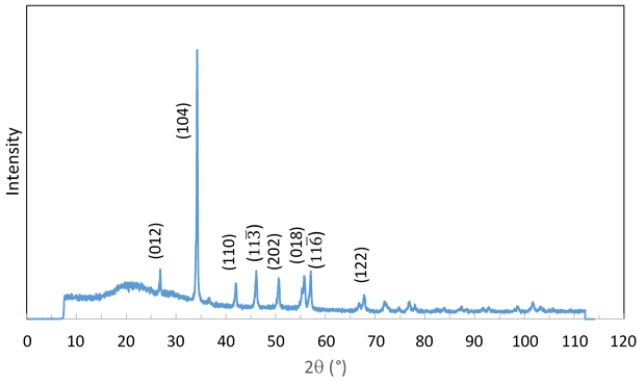

Fig. 4 XRD diffractogram on the TGA residue collected after heating up the neat BIOPLAST® GS 2189 polymer to 560°C

Rangari et al. [23] have studied the blends of BIOPLAST® GS 2189 and waste eggshell-based $CaCO_3$ nanoparticles. We remarked that their XRD patterns obtained on neat BIOPLAST® GS 2189 overlap with those obtained on $CaCO_3$ nanoparticles coming from the eggshell waste indicating the presence of $CaCO_3$ in BIOPLAST® GS 2189.

Santos et al. [22] have performed a TGA experiment by heating neat BIOPLAST® GS 2189 up to 500 °C. They have

indicated that PLA was first decomposed and starch was further decomposed above around 330 °C. They have attributed the first main peak of derivative thermogravimetric (DTG) signal to the degradation of PLA and the second main peak to that of starch and have determined a composition of around 40-45% of starch since a weight loss of 55% has been measured at the end of the PLA degradation temperature [22], [25]. On their TGA thermogram, the weight of residue at their maximum TGA temperature (500 °C) of BIOPLAST® GS 2189 was around 25% but they did not take into account the presence of mineral fillers. Teixeira et al. [20] have found 10% of starch and 90% PLA in neat BIOPLAST® GS 2189. Hassan et al. [24] have observed a maximum decomposition rate peak of BIOPLAST® GS 2189 in TGA at 342 °C and they have assigned this peak to the decomposition of PLA in BIOPLAST® GS 2189.

If we attribute the first degradation zone to PLA in our TGA thermogram and without taking into account the amount of $CaCO_3$ filler, we found 58% of PLA and the remaining weight of 42% would be starch. These results are very similar compared to the results of Santos et al. [22], [25]. Nevertheless, after PLA decomposition followed by the starch decomposition at 420 °C, the remaining weight was still around 23%. If it is assumed that this residue was totally originated from mineral filler of $CaCO_3$, then the weight of starch would then be 19% rather than 42%. It was then concluded that the BIOPLAST® GS 2189 could contain around 60% of PLA, 20% of starch and 20% of $CaCO_3$. It is also possible that the native starch includes some inorganic components [29], [30].

The spruce sawdust particles screened by a 400 µm mesh size sieve were observed by means of optical microscope and SEM (Fig. 5).

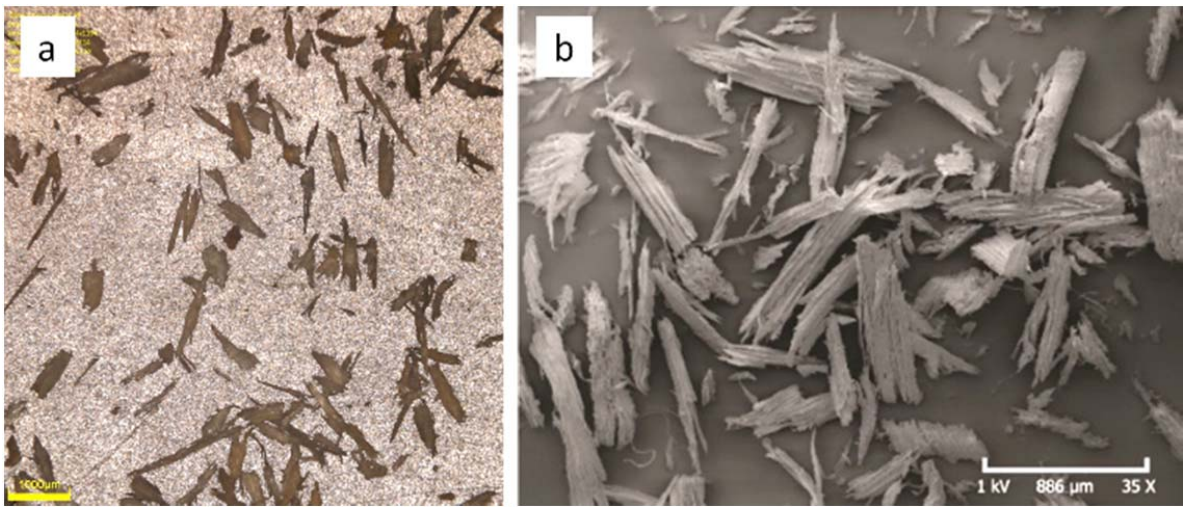

Fig. 5 Spruce wood sawdust particles observed by optical microscope (a) and SEM (b)

The size and aspect ratio of wood filler particles can play a role on the mechanical properties of filled polymers. The particle size distribution was analyzed over around hundred particles on the picture taken by optical microscope (Fig. 5 (a)). The particle size range was investigated from around 100 µm to 2000 µm by a step of 100 µm. The number of particles for each particle size range was counted (vertical left axis on Fig. 6). The cumulative number of particles was also represented (vertical right axis on Fig. 6).

As observed in Fig. 6, the majority of the particles had a size of less than 1100 µm. It was expected that the maximum particle size should be the length of the diagonal of the square mesh of sieve i.e. $400\sqrt{2}$ µm. Our particle size measurements indicate that the particles enter to the meshes vertically and most of the particles have a size smaller than 1µm.

The average aspect ratio calculated from the length to width ratio is around 4.2.

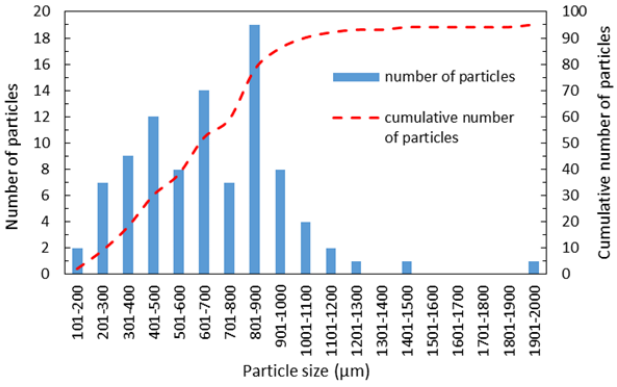

Fig. 6 Particle size distribution of used spruce sawdust

B. Characterization of Mechanical Properties

The mechanical properties of WPCs as well as neat BIOPLAST® GS 2189 were characterized by means of tensile test, three point flexural test and impact test.

The tensile test experiments were performed over 5 samples for each composition and an average value has been

accounted. The tensile test curves were plotted for different WPCs composition (Fig. 7).

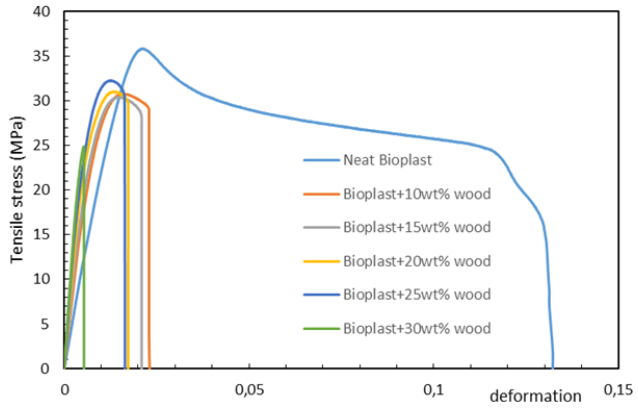

Fig. 7 Tensile test curves from the various WPC samples and neat BIOPLAST® GS 2189

On neat BIOPLAST® GS 2189 samples, an average ultimate tensile strength of 36 MPa was obtained with an average deformation value at break of around 0.13 (elongation of 13%). The filling of polymer with spruce sawdust decreased slightly the ultimate strength to around 30 MPa. The wood filled polymer composite samples had smaller deformations making it more brittle.

The tensile modulus was calculated from the initial slope of the stress-strain curves (Fig. 8). The tensile modulus seemed to increase linearly with increasing amount of wood filler in this range of filler content.

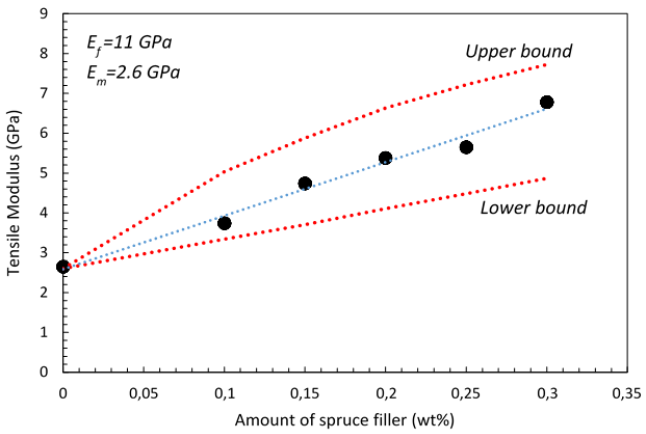

Fig. 8 Variation of the tensile modulus of BIOPLAST® GS 2189-spruce WPCs for different amount of spruce sawdust filler

On neat BIOPLAST® GS 2189, a tensile modulus of 2.6 GPa was calculated which is in agreement with the value given on the date sheet of BIOPLAST® GS 2189 supplier [18], i.e. 2.5 GPa. The bulk spruce wood material has a usual tensile modulus around 10-12 GPa [31]-[33]. Our experimental points remain between the theoretical upper and lower limits of tensile modulus calculated from the equations below [34]:

Upper bound

$$E_c = E_m V_m + E_f V_f \quad (2)$$

Lower bound

$$E_c = \frac{E_m E_f}{(V_m E_f + V_f E_m)} \quad (3)$$

where E_c,E_m, E_f, are the tensile moduli of composite, matrix and filler and V_m and V_f are the volume fraction of matrix and filler respectively.

Sykacek et al. [35] have studied the blends of softwood sawdust and some commercial biopolymers including BIOPLAST® GS 2189. They have found a tensile stress of 39.1 MPa on neat BIOPLAST® GS 2189 and on 30 wt% wood sawdust filled polymer. They have also observed a slight decrease of tensile stress to 37.8 MPa when the polymer was filled with 50 wt% sawdust. They claimed that this decrease in tensile stress at yield with increasing filler amount was not significant and would be due to a bad distribution of wood particles. They have also observed that the elongation at yield in tension decreased with incorporation of wood in polymer: An elongation of 2.4% on neat BIOPLAST® GS 2189 and 0.6% for 50 wt% wood filled polymer. They found a tensile modulus of 2.322 GPa on neat BIOPLAST® GS 2189 and 6.170 GPa while it was filled with a wood content of 50 wt% indicating the reinforcement effect of tensile properties with wood filler. Their results on tensile modulus and the tensile stress at yield were very close to our observations. Their elongation, at yield value of 0.6% when the BIOPLAST® GS 2189 filled with 50% of wood, is close to our elongation of 0.55% when the BIOPLAST® GS 2189 was filled with 30% of wood. On neat BIOPLAST® GS 2189, our elongation at break value (13%) is close to the value given on the data sheet of BIOPLAST® GS 2189 supplier (16%) [18]. The elongation at yield of 2.2% measured in our experiment on neat BIOPLAST® GS 2189 is close to the elongation at yield given by Sykacek et al. [35], i.e. 2.4%.

The rod shaped WPC samples were characterized in three point flexural test in order to evaluate the flexural Modulus of Elasticity (MOE) by using the classical equation of strength of materials applied to beams having a rectangular cross section:

$$MOE = \frac{L^3}{4\,b\,h^3}\frac{\Delta P}{\Delta f} \quad (4)$$

where ΔP and Δf are respectively the applied load and deflection at midspan and L, b, h are the span, the width and height of the sample.

The results of bending tests showed that MOE increased with increasing filler content in BIOPLAST® GS 2189 (Fig. 9). For neat BIOPLAST® GS 2189, the MOE was found around 2.1 GPa, and the flexural MOE was almost two times more important when the polymer was filled with 30 wt% spruce sawdust. The increase of flexural MOE seemed to be linear with increasing spruce sawdust filler amount.

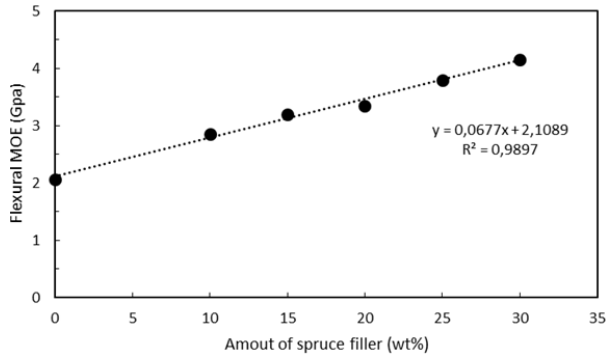

Fig. 9 Flexural MOE of BIOPLAST® GS 2189-spruce WPCs for different amount of spruce sawdust filler

The MOE calculated in our work was in agreement with the data given on the datasheet of BIOPLAST® GS 2189 (flexural modulus of 2.5 GPa) [18] and the values found in the literature [20], [35].

By using the equation of linear trend curve obtained on Fig. 9, the MOE of blank wood would be around 8.9 GPa which is in the range of MOE for spruce species found in the literature. In fact, the MOE of spruce lies between 7.1 GPa to 9.5 GPa depending on the spruce species [31], [36]. The reinforcement effect of polymer by incorporation of spruce sawdust was again confirmed in flexural mode which was also observed in tensile test in our work.

The unnotched IZOD impact tests were performed on WPCs and on neat BIOPLAST® GS 2189 for comparison. The experiments were repeated at least three times and an average value was calculated. The impact strength of the spruce sawdust filled BIOPLAST® GS 2189 samples was lower than that of neat polymer (Fig. 10).

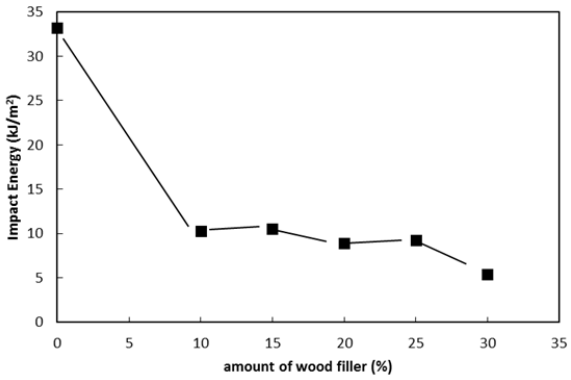

Fig. 10 Impact strength of WPCs of BIOPLAST® GS 2189 with different spruce filler amount

The impact energy for neat polymer was around 38.5 kJ/m^2 and decreased drastically to around 10.7 kJ/m^2 and 5.6 kJ/m^2 for 10 wt% and 30 wt% spruce filled polymer, respectively. These results indicated that the wood filled BIOPLAST® GS 2189 samples became more brittle compared to the neat polymer and corroborated the results of the tensile tests where the deformation was substantially decreased on wood filled BIOPLAST® GS 2189 compared to the neat one. Our results were in agreement with the results of Sykacek et al. [35] where they obtained an impact strength of 6.4 kJ/m^2 for 30% filled and 4.8 kJ/m^2 for 50% filled Bioplast.

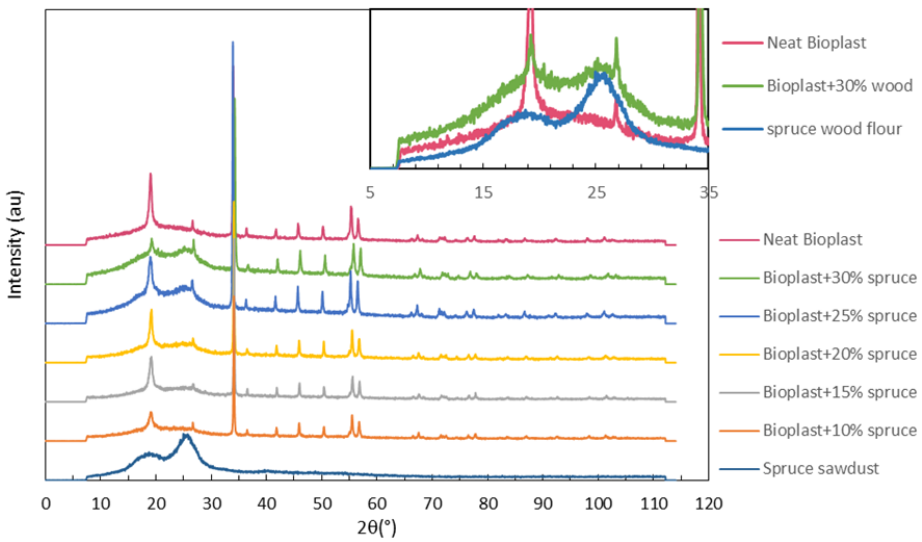

Fig. 11 XRD of WPCs with different spruce amount and raw materials (spruce sawdust and Bioplast)

C. Structural Properties

The XRD experiments were performed on WPCs with different amount of filler and on raw materials i.e. BIOPLAST® GS 2189 and spruce sawdust (Fig. 11). In the inset, the diffractograms of raw materials and 30 wt% filled polymer were displayed for finer comparison. On spruce sawdust, the XRD diffractogram showed two main broad patterns at 19.38° and 25.95° and a low intensity pattern at 40.78° in 2θ corresponding to the (101), (002) and (040) planes of cellulose [37]. On neat BIOPLAST® GS 2189, several sharp XRD diffraction patterns were detected (Fig. 11) indicating the presence of high crystallinity domains. A

main sharp pattern at around 34° in 2θ and other less intense patterns were observed at around: 26.64°, 36.38°, 41.73°, 45.72°, 50.22°, 55.27°, 56,58° and above 60° in 2θ. These patterns overlap with the diffraction patterns observed on the residue of BIOPLAST® GS 2189 heated to 560 °C in TGA (Fig. 4), indicating that the origin of these patterns was the inorganic $CaCO_3$ fillers in BIOPLAST.

The XRD pattern at around 25.95° increased as the wood sawdust was gradually added to polymer, indicating the efficient incorporation of wood into the BIOPLAST® GS 2189 (inset of Fig. 11). The sharp pattern at 19° as well as a broad peak around 22° in 2θ would probably be in relation with crystalline and amorphous part of Bioplast respectively. In fact, native starch has relatively sharp XRD patterns between 17.5° and 29° in semi crystalline form [38] but when heated to around 210-230 °C, its degree of crystallinity decreases or totally lost [39]. PLA has a main sharp peak at 19.1°-19.7° [40], [41] as well as an amorphous halo and can be considered as a semi crystalline polymer [40].

Rangari et al. [23] have observed several XRD patterns on neat BIOPLAST® GS 2189 polymers with two main peaks at around 19.4° and 34,3° which would correspond to our two main patterns. Our diffractogram on neat BIOPLAST® GS 2189 matched up to almost all XRD pattern positions found in the literature [23] [24].

D. Thermal Properties

The thermal properties of wood BIOPLAST® GS 2189 composites were studied by TGA and DSC analysis.

The TGA analysis was performed on the spruce sawdust filled BIOPLAST® GS 2189 samples as well as the raw materials: neat BIOPLAST® GS 2189 and spruce sawdust (Fig. 12). The TGA thermogram of neat BIOPLAST® GS 2189 was studied at the previous section (Fig. 2). The spruce sawdust showed a maximum degradation rate at around 360 °C. The degradation temperatures of WPCs seemed to be higher than that of neat BIOPLAST® GS 2189 at least up to the temperature of approximately 350 °C (i.e. from a weight of 97% to around 40%). We also noticed that the degradation temperature shifted to the higher values with increasing spruce sawdust amount in WPCs. These observations would indicate that the spruce sawdust delays the thermal degradation of neat BIOPLAST® GS 2189 and WPCs are thermally more stable than the neat polymer. A shift to the higher values of the degradation temperature has already been reported for BIOPLAST® GS 2189 filled with multiwalled carbon nanotubes (CNT) [23] or eggshell based $CaCO_3$ nanoparticles [24].

The residue weight at the end of the TGA experiments, at 800 °C, was around 12% on neat BIOPLAST® GS 2189 and slightly higher on WPCs and raw spruce sawdust.

After erasing the thermal history of the polymer by a first heating, the DSC experiment was plotted for the second heat scan. The second heat DSC curve on the neat BIOPLAST® GS 2189 sample showed a small change at around 55 °C, an exothermic peak around 108 °C and a doublet of endothermic peaks at around 143 and 152 °C (Fig. 13). Similar shape of DSC thermogram has been observed and attributed to the glass transition (T_g), cold crystallization (T_c) and melting (T_m) in BIOPLAST® GS 2189 [22], [24]. Santos et al. [22] proposed that the starch contained in BIOPLAST® GS 2189 did not show any visible melting peak in the temperature range used (20-200 °C) indicating that it has an amorphous structure, then only the PLA thermal properties are considered.

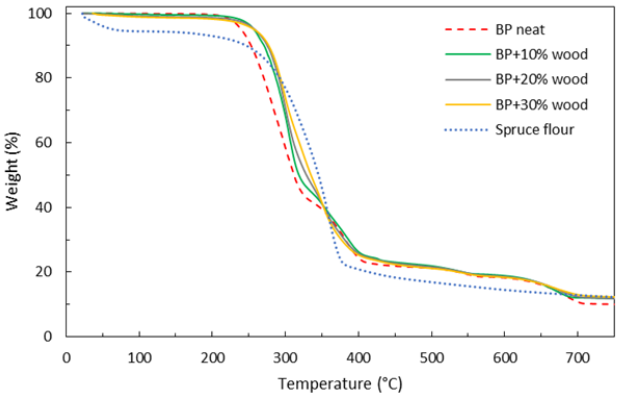

Fig. 12 TGA of WPCs filled as well as raw materials of BIOPLAST® GS 2189 (BP) and spruce sawdust

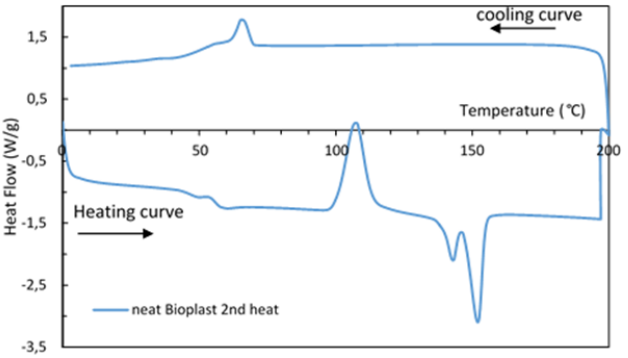

Fig. 13 DSC of neat BIOPLAST® GS 2189

A doublet of melting peak has been observed on the biodegradable pots manufactured with BIOPLAST® GS 2189 by injection and the presence of double melting peak was interpreted as the possibility of the crystal clusters formation [22]. The injection process has induced the degradation of polymer by decreasing the molecular weight (Mw) of polymer either by shear forces in injection process or the thermal sensitivity of PLA [22]. During the cooling cycle, a peak at around 67 °C was detected in DSC and identified as the crystallization peak [22], [24].

When the BIOPLAST® GS 2189 was filled with spruce sawdust, the T_g, T_c and T_m of WPCs shifted to higher temperature (Fig. 14), for example the T_g, T_c and T_m (for main melting peak) are 55.5, 108.5 and 152 °C on neat polymer and 56.2, 113.8 and 156 °C on 30 wt% wood filled polymer, respectively.

The same trend has been reported on BIOPLAST® GS 2189 filled either with CNTs [23] or eggshell-based $CaCO_3$

nanoparticles [24].

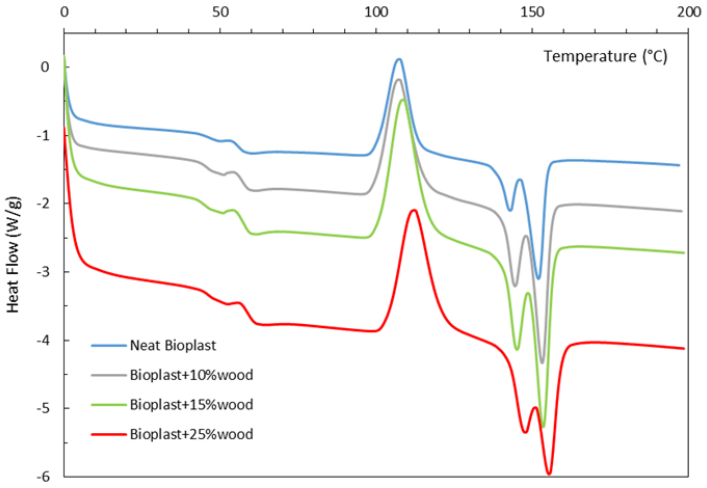

Fig. 14 DSC thermograms of WPCs in second heating scan and neat BIOPLAST® GS 2189

E. Melt Flow Index

For neat BIOPLAST® GS 2189, MFI was found to be around 44. The MFI of WPCs decreased with increasing spruce sawdust filler content (Fig. 15). For 30 wt% filled polymer, the MFI of WPC was around 4.2.

The MFI (in g/10 min) is defined as:

$$MFI = \frac{0.0495\, W\, \rho}{\eta_0} \quad (5)$$

where W is the test load (in g), ρ is the specific gravity (g/cm^3) and η_0 is the viscosity at zero shear (poise) [42], [43]. The MFI is proportional to the specific gravity and inversely proportional to the viscosity. When the neat polymer was filled with 30 wt% of spruce sawdust, its specific gravity decreased from 1.35 to 0.75 g/cm^3 i.e. less than 2 times; nevertheless MFI decreased almost 10 times (Fig. 15). This observation would indicate that the decrease in MFI with increasing amount of wood filler was mostly due to the increase of viscosity in WPCs rather than the decrease of the specific gravity.

F. Color Measurement

The color can be important for specific applications of WPCs like decoration where the aesthetic appearance is critical for the consumer.

The incorporation of spruce sawdust into BIOPLAST® GS 2189 modifies the sample color. Visual color inspection was made on the WPC specimens (sample pictures from 0 to 30 wt% shown in Fig. 16).

The color can be important for specific applications of WPCs like decoration where the aesthetic appearance is critical for the consumer.

In order to observe changes in the color of WPCs specimens quantitatively, the L*, a* and b* parameters were measured and their evolution for different amount of spruce sawdust filler was plotted (Fig. 16).

While filling the polymer with spruce sawdust, L* parameter is decreasing and a* and b* parameters are increasing, indicating that the WPCs become darker, more reddish and yellowish.

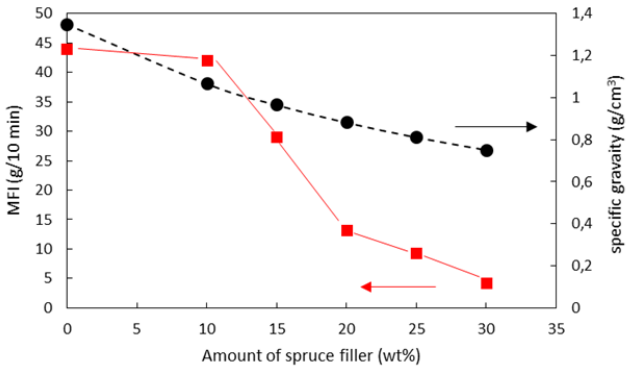

Fig. 15 Evolution of MFI and specific gravity of WPCs with different amount of spruce sawdust filler

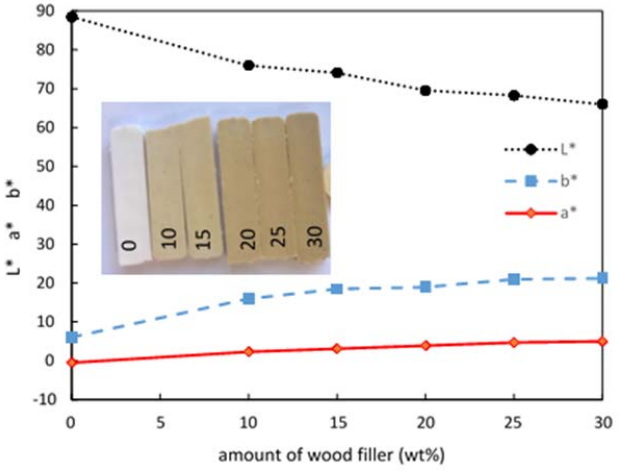

Fig. 16 L*, a* and b* color measurement on WPCs. The specimen for color measurements are shown in the inset with indicated amount of filler (wt%)

G. Water Absorption

The moisture content of neat BIOPLAST® GS 2189 mentioned on the product datasheet is < 0.2 wt% [18]. The incorporation of wood into the polymer can change the sensibility of WPCs with respect to the WA.

The water absorption (WA in %) was calculated from the expression of Mass Change (1) with m_0 is the initial dried mass, and m is the mass at any instant. Its evolution with time was plotted as a function of cumulative immersion time in distilled water for WPCs as well as the neat BIOPLAST® GS 2189 and the bulk spruce samples (Fig. 17). The WA increased with immersion time on all samples within the scheduled time of around 140 h. For a given time, the more the WPC specimen contained the spruce wood sawdust, the more the WA was important. The WA was around 0.3% on neat BIOPLAST® GS 2189 after 24 hours of immersion at room temperature.

The WPCs filled with 30 wt% of wood absorbed 2,8% of water after 24 hours however the bulk spruce specimens used as wood reference absorbed up to 138% (Fig. 17, red dots with right axis). The WA on the filled BIOPLAST® GS 2189 with the highest amount of wood filler in our experiments (30 wt%) was almost 50 times less than that on bulk spruce samples after 24 h of immersion in water.

The evolution of WA with time was modelized with a power function of time [44] [45]:

$$WA = kt^n \tag{6}$$

For the neat BIOPLAST® GS 2189 and all the WPCs except that of 30 wt%, the experimental WA curves were fitted with a power of n=0.5, indicating that the absorption obeys the Fick diffusion law [44]. On the inset of Fig. 17, the fitted curve (dotted line) is shown with the experimental results obtained on 10 wt% filled BIOPLAST® GS 2189. On 30 wt% wood filled WPC, the WA rate seemed to be faster with a power of approximately 0.7 meaning an anomalous transport mechanism [44]. In fact, on the surface of 30wt% wood filler samples, the cracks were observed at the end of the water immersion experiments.

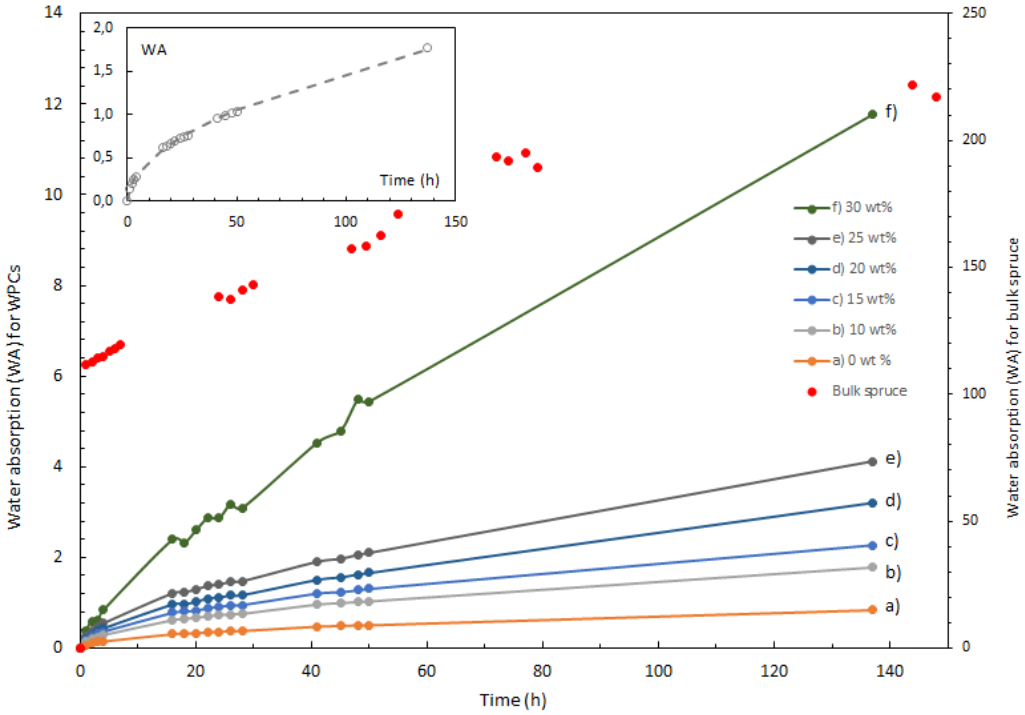

Fig. 17 The WA with respect to the cumulative immersion time at room temperature for WPCs (left axis). For comparison spruce specimens have also studied (right axis). In the inset, the experimental values of water uptake (open dots) fitted with a square root function of time (dotted line) is plotted on 10wt% of wood incorporated BIOPLAST® GS 2189

BIOPLAST® GS 2189 is a blend of PLA and starch and our WPCs include also wood particles. Starch is hydrophilic, but PLA is a hydrophobic polymer [46]. When starch is soaked in excess water at 25 °C, it can take up to about 50% water on a dry weight basis [46]. The spruce bulk specimens absorbed more than 200% after 140 h soaking in water. In neat BIOPLAST® GS 2189, even with an estimated starch amount of around 20 wt%, the WA was less than 1% after 140 h immersion. For 30 wt% spruce incorporated WPCs, the WA was less than 12%. These observations would indicate that the starchy zones as well as the spruce sawdust particles were protected by PLA.

Sykacek et al. [35] have found a water uptake of 0.203% on neat BIOPLAST® GS 2189 and respectively 1.181% and 2.099%, on 30% and on 50% wood filled BIOPLAST® GS 2189 after 24 h. BIOPLAST® GS 2189 contains also $CaCO_3$ and the presence of mineral fillers like $CaCO_3$ particles decreases the water uptake in WPCs [47]. The wood sawdust

decreased the water resistance of all WPCs compared to the neat polymer because of the higher hygroscopic nature of wood compared with the neat polymer reference.

H.Termite and Fungal Resistance

WPCs samples were exposed to termites (*Reticulitermes flavipes ex. santonensis*) in non-choice screening test with respect to the EN117 standards. Beech and pine samples were used as reference for comparison with WPC samples.

The degradation due to the termites was visually rated according to the criteria of EN117(2013) which is adjusted for sample size. The samples are shown on Fig. 18.

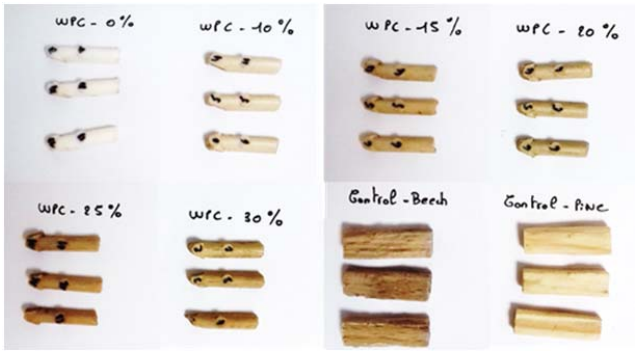

Fig. 18 Visual appearance of Wood Polymer Composites and Control samples after *Reticulitermes flavipes* termite exposure.

The Mass Loss (ML%) due to the termites exposure was calculated by weighing the anhydrous masses before and after experience by using Mass Change in (1). Table II shows the termite exposure test results. SD represents the standard deviation.

TABLE II
AVERAGE VALUES OF ML (%), TERMITE SURVIVAL RATES AND VISUAL RATING AFTER TERMITE RESISTANCE TESTS

wt% wood	Average ML (%)	SD (%)	Visual rating
0	0,39	0,002	1
10	0,71	0,102	1
15	0,96	0,192	1
20	1,39	0,086	1
25	1,40	0,497	1
30	2,72	0,739	2
Control samples			
Beech	12,90	0,942	4
Pine	19,08	3,763	4

The ML calculated from (1) was very small on neat BIOPLAST® GS 2189 and increased with increasing amount of spruce filler. Nevertheless the ML was lower on WPCs compared to the beech and pine wood control samples. With beech and pine control samples, the mortality of termites was less than 50% and the degree of attack was 4, which allows to validate the termite resistance test. All the WPC samples studied in this work were quoted 1 in visual rating (attempted attack), except that the WPC with the highest spruce sawdust content (30 wt%), rated 2 (slight attack).

The resistance of WPCs to fungal attacks to two brown-rots [CP; PP] and one white-rot [CV] was examined and the conditions were detailed in the experimental section. The control samples of beech (*Fagus sylvatica*) and pine sapwood (*Pinus sylvestris*) were inserted into each test device (Fig. 19). The ML due to the fungal attack was calculated by using the Mass Change equation (1). The beech and pine is in class 4, as slightly durable (15 < ML (%) < 30) as shown on Table III.

Fig. 19 Screening fungal test devices (*ex: PP*) for Wood Polymer Composite samples and pine wood controls

TABLE III
AVERAGE VALUES OF ML OF BEECH AND PINE CONTROL SAMPLES ACCORDING TO THE THREE TESTED FUNGUS, AND DECAY RESISTANCE VALIDATION TEST CONDITIONS RELATIVE TO XP CEN/TS 15083-1 (2006).

	ML minimal average values of control samples, required in XP CEN/TS 15083-1 (2006)	
Degradation source	Control samples associated to WPC samples	in % (m/m)
Brown rot on *Pinus sylvestris*		
Coniophora Putena	31.65	30
PP	56.56	20
White rot on *Fagus sylvatica*		
CV	20.62	20

The ML due to the fungal exposure on WPCs was tabulated on Table IV and the classification of WPCs decay resistances was determined by using Table I. The average ML increased with increasing amount of spruce sawdust in BIOPLAST® GS 2189 for two brown-rots (CP and PP) and one white rot (CV). Nevertheless the ML remained below 5% in median value, indicating that all the WPCs samples were classified 1 in durability class, i.e. very durable to fungal attacks. According to the ML values obtained concerning the fungal degradation of beech and pine wood control samples, the decay resistance test performed through this study was validated. Indeed, in accordance with Table III, the minimal degradation level of control samples were reached.

TABLE IV
MEAN AND MEDIAN VALUES OF ML FOR ALL EXPOSED WPC SAMPLES AND PROVISIONAL NATURAL DURABILITY CLASS OF THE TESTED WPC ACCORDING TO XP CEN/TS 15083-1 (2006)

wt% wood	Average ML (%)	Median Value of average loss (%)	SD (%)	Durability Class[a]
		CP		
0	0.54	0.51	0.14	1
10	0.87	0.88	0.12	1
15	0.98	1.01	0.14	1
20	1.27	1.28	0.28	1
25	1.65	1.57	0.49	1
30	2.53	1.68	2.37	1
		PP		
0	0.06	0.00	0.08	1
10	0.19	0.24	0.12	1
15	0.48	0.48	0.21	1
20	0.89	1.02	0.24	1
25	1.09	1.04	0.25	1
30	1.24	1.13	0.31	1
		CV		
0	0.33	0.25	0.15	1
10	0.51	0.48	0.08	1
15	0.58	0.56	0.11	1
20	0.68	0.64	0.19	1
25	0.90	0.80	0.33	1
30	1.06	0.90	0.36	1

[a]Refer to XP CEN/TS 15083-1 (2006)

IV. CONCLUSIONS

The WPCs were elaborated by blending BIOPLAST® GS 2189, a biopolymer (including PLA and potato starch) and spruce sawdust with a maximum filler amount of 30 wt%. Since both components are bio based, the resulting composites are fully ecological. Several properties of these WPCs were characterized. It was found that the neat polymer, BIOPLAST® GS 2189, contained around 60% of PLA, 20% of starch and 20% of $CaCO_3$.

The tensile and flexural modulus increased with increasing spruce sawdust amount in polymer. For neat and 30 wt% wood filled polymer, the tensile modulus was around 2.6 GPa and 6.8 GPa respectively.

The neat BIOPLAST® GS 2189 had a flexural MOE of around 2.1 GPa, and around 4.1 GPa when it was filled with 30 wt% spruce sawdust. The ultimate tensile strength of 36 MPa was obtained with an average deformation value at break of around 0.13 on neat polymer. The filling of polymer with spruce sawdust decreased slightly the ultimate strength to around 30 MPa. The wood filled polymer composite samples had smaller deformations (0.05 for 30 wt %) thus became more brittle. This observation was confirmed by IZOD impact test where the impact energy decreased with increasing spruce sawdust amount.

WPCs are thermally more stable than the neat polymer, since their degradation temperature shifted to higher values with increasing spruce sawdust amount in WPCs. These observations would indicate that the spruce sawdust delays the thermal degradation of neat BIOPLAST® GS 2189.

When the BIOPLAST® GS 2189 was filled with spruce sawdust, the glass transition, cold crystallization and melting temperatures of WPCs shifted to higher temperatures.

The color measurements showed that L* decreases however a* and b* increase with increasing wood filler content in WPC indicating that the WPCs became darker, more reddish and yellowish by incorporation of wood.

The water adsorption was correlated to the proportion of wood in WPCs. The WA was around 2.8% on WPCs having the highest amount of woof filler in this work (30 wt% spruce) after 24 hours of immersion at room temperature. Moreover the WA on WPCs was always much less than the bulk spruce used as a control sample indicating that the WPCs were more resistant to WA compared to bulk spruce.

The termite and fungal resistance tests on WPCs showed that the resistance decreased with increasing spruce amount in WPCs. All the WPCs were quoted 1 in visual rating (attempted attack), except that the WPC with 30 wt% wood, rated 2 (slight attack) concerning termite resistance. The WPCs were found in the durability class 1 regarding to the fungal resistance indicating that they are very durable.

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